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Synthesis of 1,3-Dichloro-*cyclo*-1,3-diphosphadiazanes from Silylated Amino(dichloro)phosphanes

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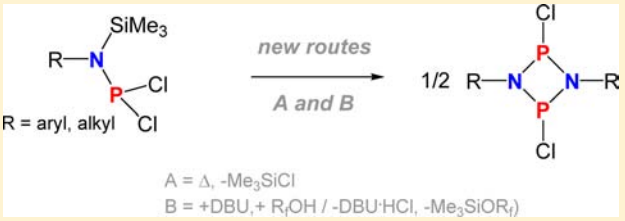
Supporting Information

ABSTRACT: The synthesis of 1,3-dichloro-*cyclo*-1,3-diphosphadiazanes $[ClP(\mu\text{-}NR)]_2$ via elimination of Me_3SiCl from silylated amino(dichloro)phosphanes, $R{-}N(SiMe_3)PCl_2$, was studied by different synthetic protocols starting from $R{-}N(H)SiMe_3$ (R = $Si(SiMe_3)_3$ = Hyp, $N(SiMe_3)_2$, Mes* = 2,4,6-tri-*tert*-butylphenyl, Ter = 2,4-bis(2,4,6-trimethylphenyl)phenyl, Dipp = 2,6-diisopropylphenyl, Dmp =2,6-dimethylphenyl, Ad = Adamantyl, Trityl = Ph_3C, Tos = tosyl = $CH_3C_6H_4SO_2$, *n*-Oct = *n*-octyl, and Me_3Si).

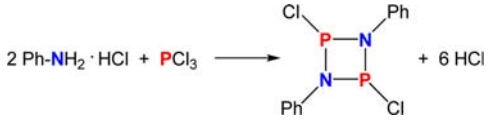


A new synthetic route using trimethylsilyl-substituted amino(dichloro)phosphanes, $R{-}N(SiMe_3)PCl_2$, was developed to form *cyclo*-diphosph(III)-azanes simply by adding a mixture of R_fOH/base (R_fOH = hexafluoroisopropanole). By this method electron-rich/-poor aryl-, silyl-, and bissilylamino-substituted *cyclo*-diphosph(III)-azanes are accessible such as the unprecedented $(Me_3Si)_2N$-substituted species $[ClP(\mu\text{-}NN(SiMe_3)_2)]_2$ starting from tris(trimethylsilyl)hydrazine and PCl_3. Additionally, the difficulties with the preparation of *cyclo*-diphosphadiazanes depending on the starting materials, solvents, and bases due to the competition of different reaction channels are studied.

INTRODUCTION

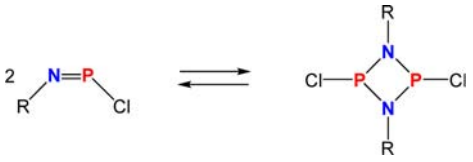
Four-membered phosphorus−nitrogen heterocycles of the type $[XP(\mu\text{-}NR)]_2$ (X = halogen, amino group, organic substituent) are known as *cyclo*-1,3-diphospha(III)-2,4-diazanes (short *cyclo*-diphosphadiazanes, old name: 1,3-diaza-2,4-diphosphetidines).[1] As early as 1894 Michaelis and Schroeter described the first phosphorus(III)−nitrogen heterocycle which they obtained from the reaction of aniline hydrochloride with an excess of PCl_3 (Scheme 1).[2] Interestingly, the authors assumed to have

Scheme 1. First Synthesis of a *cyclo*-1,3-Diphospha(III)-2,4-diazane



generated monomeric $C_6H_5{-}N{=}P{-}Cl$, which they called "phosphazobenzolchlorid". However, since their molecular weight measurements agreed with the double mass, they speculated on the existence of the dimer (Scheme 2). Today we know that the dimeric four-membered ring system is the stable form. Later it was shown that this reaction results in the formation of the corresponding bis(dichloro)phosphanephenylamine, $Ph{-}N(PCl_2)_2$, rather than the four-membered ring.[3] However, the *cyclo*-diphosphadiazane is formed upon thermal elimination of PCl_3 from $Ph{-}N(PCl_2)_2$. *cyclo*-Diphosphadiazanes play a major role in preparative phosphorus−nitrogen chemistry because such species are good starting

Scheme 2. Dimerization of Iminophosphanes



materials for (poly)cyclic inorganic and organometallic compounds.[4−6]

Depending on the organic group R, the solvent, and the state of aggregation, 1,3-dichloro-*cyclo*-diphosphadiazanes, $[ClP(\mu\text{-}NR)]_2$, display a monomer−dimer equilibrium between R−N = P−Cl (iminochlorophosphane) and $[ClP(\mu\text{-}NR)]_2$, which was addressed in a series of papers.[7,8] For example, Burford et al. proposed that, dependent upon steric hindrance in derivatives of $[XP(\mu\text{-}NR)]_2$, the dimer can be destabilized with respect to the monomer.[8] For instance, for Mes*N=P−Cl (Mes* = 2,4,6-tri-*tert*-butylphenyl) with bulky Mes* substituent the iminophosphane monomer is observed in the solid state,[9] while slightly smaller substituents such as 2,6-diisopropylphenyl or *m*-terphenyl [Ter = *m*-terphenyl = 2,6-bis-(2,4,6-trimethylphenyl)] allow dimerization.[1,4,8]

Scheme 3 summarizes different synthetic routes to *cyclo*-diphosphadiazanes. The simplest *cyclo*-diphosph(III)azanes are the dichloro derivatives, $[ClP(\mu\text{-}NR)]_2$ (compound **3**), which can be readily synthesized by reaction of a primary amine with

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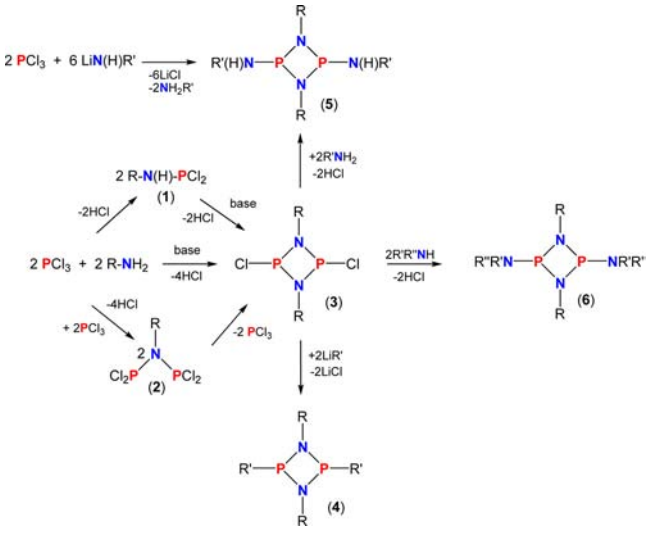
Scheme 3. Synthetic Strategies to *cyclo*-1,3-Diphospha(III)-2,4-diazanes



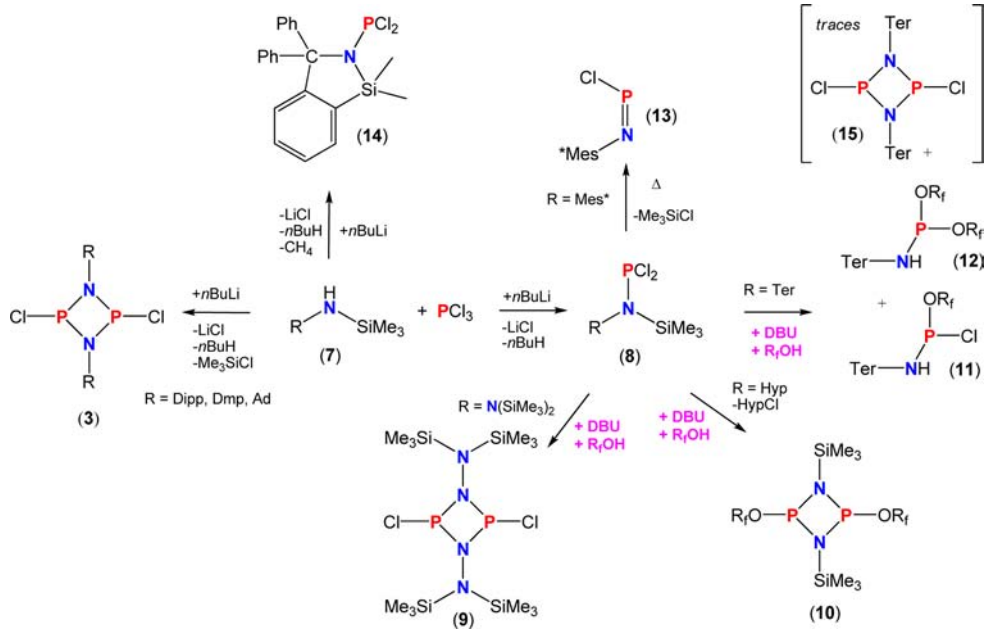
PCl_3.[1] Depending on the stoichiometry, the amount and kind of base, solvent, temperature, etc., the reaction can be carried out stepwise either via aminobis(dichloro)phosphanes **2** or amino(dichloro)phosphanes **1**.[10] These reactions might be regarded as sequential dehydro-chloride metathesis or in general as a cyclocondensation process. Conversion of **1** and **2** into *cyclo*-diphosphazanes (**3**) can easily be achieved under mild conditions.[11] Bis(organylamino) derivatives (**5** or **6**) are obtained by treatment of **3** with primary and secondary amines, respectively, or in one-pot reactions of PCl_3 with an excess of amine. The heterosubstituted derivatives (**4** and **5**) are prepared by reaction of **3** with organolithium compounds or when PCl_3 is treated with an excess of lithium amides. Problems, which are often encountered, are the formation of side products such as $Cl-P[N(H)R]_2$ or $P[N(H)R]_3$,[10] low yields due to a poor selectivity, and the formation of large amounts of hydrochlorides which often do not allow follow-up chemistry. Therefore, we report herein on our search for a selective synthetic route (Scheme 4), which avoids the formation of HCl by utilizing trimethylsilyl-substituted amino(dichloro)phosphanes, $R-N(SiMe_3)PCl_2$. Silylated aminodichlorophosphanes are capable of intrinsically releasing Me_3SiCl, thus forming an iminochlorophosphane (Scheme 2) and finally *cyclo*-diphosphazanes upon dimerization. Romanenko et al. and Klusmann et al. already reported on such Me_3SiCl elimination reactions leading to the desired dimers $[ClP(\mu\text{-}NR)]_2$ (for R = *t*-Bu, Trip = 2,4,6-triisopropylphenyl) or monomeric Mes*NPCl, respectively.[12−14] In this work we show that, alternatively, the conversion to *cyclo*-diphosphazanes can be achieved simply by adding a mixture of R_fOH/base (base = DBU = 1,8-diazabicyclo[5.4.0]undec-7-en). By these two methods, electron-rich/-poor aryl-, silyl-, and bissilylamino-substituted *cyclo*-diphosphazanes are accessible. Here we report on the scope and advantages of this novel approach to *cyclo*-diphosphadiazanes.

RESULTS AND DISCUSSION

As illustrated in Scheme 4, the synthesis of *cyclo*-diphosphadiazanes $[R'P(\mu\text{-}NR)]_2$ (often only *in situ* generated) *via* silylated amino(dichloro)phosphanes, $R-N(SiMe_3)PCl_2$ (**8**), has been studied starting from $R-N(H)SiMe_3$ (**7**) [R = Hyp = $Si(SiMe_3)_3$,[15] $N(SiMe_3)_2$,[16,17] Mes*,[7d,9] Ter,[18−20] Dipp = 2,6-diisopropylphenyl,[21] Dmp = 2,6-dimethylphenyl, Ad = adamantyl, trityl = Ph_3C, Tos = tosyl = $CH_3C_6H_4SO_2$, *n*-Oct = *n*-octyl, and Me_3Si[22]]. The corresponding silylamines $R-N(H)SiMe_3$ can easily be obtained starting from the amine $R-NH_2$ in the reaction with *n*-BuLi and Me_3SiCl (see Supporting Information).[23]

Synthesis. Synthesis of **3**Dipp, **3**Dmp, and **3**Ad was achieved when to a stirred solution of $R-N(SiMe_3)H$ (R = Dipp, Dmp, Ad) in Et_2O was added *n*-BuLi dropwise at ambient temperature, followed by addition of PCl_3 at −30 °C over a period of 20 min. Presumably, *in situ* formation of $R-N(SiMe_3)PCl_2$ (**8**) occurred which finally reacted to **3**Dipp,

Scheme 4. Synthesis of *cyclo*-Diphosphazanes Utilizing Silylated Amines



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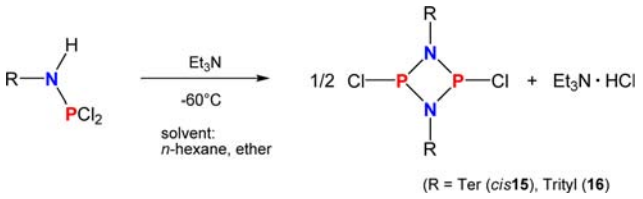
3Dmp, and 3Ad upon thermal elimination of Me_3SiCl at ambient temperature (Scheme 4). The same protocol leads to a totally different product for the trityl-substituted species $Ph_3C-N(SiMe_3)H$. *In situ* generated $Ph_3C-N(SiMe_3)PCl_2$ releases methane while a $Si-C_{phenyl}$ bond is formed leading to the bicyclic product **14** (Scheme 4). However, trityl-substituted *cyclo*-diphosphadiazane, $[ClP(\mu\text{-}NCPh_3)]_2$ (**16**, Scheme 5), was

Scheme 5. Synthesis of Ter- and Trityl-Subsituted *cyclo*-Diphosphadiazanes



obtained by the conventional two-step procedure when $Ph_3C-N(H)PCl_2$ was treated with NEt_3 in diethyl ether at −60 °C. Obviously, there are two different competing thermal processes for $Ph_3C-N(SiMe_3)PCl_2$, which might be caused by steric or electronic features of the ligand. However, no simple explanation can be given for the preference of CH_4 versus Me_3SiCl elimination. It should be noted that the synthesis and structure of 3Dipp, obtained from $DippNH_2$ and PCl_3 in the presence of Et_3N, was reported by the Burford group (Scheme 1).[10]

Stable silylated amino(dichloro)phosphanes, $R-N(SiMe_3)-PCl_2$ (8R), can be isolated for R = $N(SiMe_3)_2$, Hyp, and Ter. 8Mes* is only stable over several days at low temperature (−60 °C); storage at ambient temperature triggers the Me_3SiCl elimination resulting in the formation of monomeric imino-chlorophosphane **13** (Scheme 4). This behavior is in contrast with that of the arsenic analogue $Mes^*-N(SiMe_3)AsCl_2$ reported by Burford et al., which does not intrinsically eliminate Me_3SiCl at ambient temperatures.[24,25] For 8Hyp, 8Ter, and $8N(SiMe_3)_2$ no spontaneous Me_3SiCl elimination was observed at ambient temperatures. 8Ter is also very robust against water or strong acids (HCl/HNO_3). Decomposition is only observed upon thermal treatment, which goes along with the formation of undefined products. Therefore, a strong base such as DBU and hexafluoroisopropanole (R_fOH) was used to initiate a formal Me_3SiCl elimination due to elimination of DBU·HCl and the ether Me_3SiOR_f. Finally, we added DBU along with R_fOH which now gives for $8N(SiMe_3)_2$ the desired *cyclo*-diphosphadiazane **9** (Scheme 4). It is noteworthy that even methanol can be utilized as weak acid using this protocol. In contrast, for 8Hyp hypersilylchloride elimination (instead of Me_3SiCl) was observed leading to the formation of hexafluoroisopropoxy-substituted *cyclo*-diphosphadiazane **10**. For 8Ter only hexafluoroisopropoxy-substituted species such as $Ter-N(H)P(OR_f)Cl$ (**11**) and $R-N(H)P(OR_f)_2$ (**12**) were isolated. Small amounts of of *trans*-$[ClP(\mu\text{-}NTer)]_2$ (*trans*15) could be isolated and fully characterized, but the diphospha-diazane is only a minor byproduct using this synthetic method. Interestingly, a mixture of *cis/trans*-$[ClP(\mu\text{-}NTer)]_2$ is formed in good yields (83%) when Et_3N is added to a solution of $Ter-N(H)PCl_2$ in *n*-hexane (Scheme 5).[26]

Also, the reaction of $Ph-N(SiMe_3)H$ with PCl_3 in the presence of *n*-BuLi leads to different products. From the reaction mixture colorless crystals of $[Cl_2PN(Ph)P(\mu\text{-}NPh)]_2$ (**17**) along with *N*-phenyl-*N*-trimethylsilylamino-*n*-butylchlor-ophosphane $Ph-N(SiMe_3)P(n\text{Bu})Cl$ (**18**) could be separated by distillation (Kugelrohr).

The reaction of $Tos-N(SiMe_3)H$ and $n\text{-Oct}-N(SiMe_3)H$, respectively, with *n*-BuLi/PCl_3 resulted in a mixture of several products, which could not be separated by usual methods such as distillation (Kugelrohr) or fractional crystallization.

Properties and Structure. *cyclo*-Diphosphadiazanes can easily be recrystallized from *n*-hexane or CH_2Cl_2. Melting points, ^{31}P NMR data, and yields are summarized in Table 1.

Table 1. Melting Points (°C), ^{31}P NMR Data, and Yields

$[R'P(\mu\text{-}NR)]_2$	MP (°C)	*cis/trans* ratio (%)	$\delta[^{31}P]$ *cis*	$\delta[^{31}P]$ *trans*	yield (%)
$[ClP(\mu\text{-}NN(SiMe_3)_2)]_2$ (**9**)	140	87/13	212	308	71
$[R_fOP(\mu\text{-}NSiMe_3)]_2$ (**10**)		46/54[c]	174	265	67
$[ClP(\mu\text{-}NDipp)]_2$ (3Dipp)	216	99/1	211	292	83
$[ClP(\mu\text{-}NDmp)]_2$ (3Dmp)	115	93/7	210	296	86
$[ClP(\mu\text{-}NAd)]_2$ (3Ad)	263[a]	100/0	206		76
$[ClP(\mu\text{-}NCPh_3)]_2$ (**16**)	248[a]	100/0	198		80
$[ClP(\mu\text{-}NPh)]_2$[11a]	153	100/0	200		69
$[ClP(\mu\text{-}NTer)]_2$ (*trans*15)		5/95	227[b]	264[b]	
$[Cl_2PN(Ph)P(\mu\text{-}NPh)]_2$ (**17**)	155	0/100		157; 176[d]	56

[a]Decomposition. [b]The *cis* isomer can be obtained in the reaction of $Ter-N(H)-PCl_2$ with Et_3N in *n*-hexane,[26] while the reaction according to Scheme 4 yields exclusively small amounts of the *trans* isomer as byproduct. [c]*cis* = 100%; reaction condition, −50 °C. [d]157 ppm, endocyclic P; 176 ppm, exocyclic P.

The overall yields for all considered species are good. The lowest melting points are found for $[ClP(\mu\text{-}NDmp)]_2$ with 115 °C, $[ClP(\mu\text{-}NN(SiMe_3)_2)]_2$ with 140 °C, $[ClP(\mu\text{-}NPh)]_2$ with 153 °C,[11a] and $[Cl_2PN(Ph)P(\mu\text{-}NPh)]_2$ with 155 °C, while all other compounds decompose around 250 °C.

While for $[ClP(\mu\text{-}NN(SiMe_3)_2)]_2$ and $[R_fOP(\mu\text{-}NSiMe_3)]_2$ mixtures of the *cis/trans* isomers were isolated, all other studied *cyclo*-diphosphadiazanes could be obtained as almost pure *cis* isomers ($[ClP(\mu\text{-}NR)]_2$, R = Dipp, Dmp, Ad, Ph_3C, Ph) or *trans* isomers ($[ClP(\mu\text{-}NTer)]_2$ and $[Cl_2PN(Ph)P(\mu\text{-}NPh)]_2$) as displayed by ^{31}P NMR investigations (Table 1). It is interesting to note that for both isomers always only one ^{31}P resonance in solution is observed. The assignment of the ^{31}P NMR shifts was carried out on the basis of theoretically obtained values (see Supporting Information, Table S23). The $\delta^{31}P$ values of the *cis* isomers are shifted upfield compared to the *trans* isomers (*e.g.*, $[ClP(\mu\text{-}NN(SiMe_3)_2)]_2$; *cis* 212 *vs trans* 308 ppm). Also, the chemical shift within the series of different *cis* or *trans* species strongly depends on the substituents. For instance, a downfield shift is observed for *cis*-$[ClP(\mu\text{-}NTer]_2$ with 227 ppm compared to 174 ppm for *cis*-$[R_fOP(\mu\text{-}NSiMe_3)]_2$. The resonance of the *trans* chloro species is observed between 264 and 308 ppm. For comparison, the starting materials, aminophosphanes and hydrazinophosphanes, respectively, are detected between 150 and 180 ppm which lies in the range expected on the basis of numerous data from the literature for aminophosphanes (cf. 165 ppm for $(Me_3Si)_2N-N(SiMe_3)PCl_2$, 155 ppm for Dipp-N(H)$PCl_2$, 165 ppm for Dipp-$N(PCl_2)_2$, Dipp = 2,6-diisopropylphenyl).[10,17] The

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Table 2. Crystallographic Details of Compounds 9, 10, 15, and 17

	9	10	15	17
chem formula	$C_{12}H_{36}Cl_2N_4P_2Si_4$	$C_{12}H_{20}F_{12}N_2O_2P_2Si_2$	$C_{48}H_{50}Cl_2N_2P_2$	$C_{24}H_{20}Cl_4N_4P_4$
fw (g mol^{-1})	481.65	570.42	787.74	630.12
color	colorless	colorless	colorless	colorless
cryst syst	monoclinic	monoclinic	orthorhombic	triclinic
space group	*P*2/*n*	*C*2/*c*	*Fdd*2	$P\bar{1}$
a (Å)	13.0246(5)	20.2530(16)	21.9363(16)	9.3256(4)
b (Å)	15.6553(6)	8.7053(7)	44.948(3)	9.3338(4)
c (Å)	13.0864(5)	13.4567(11)	8.5007(5)	17.1117(7)
α (deg)	90.00	90.00	90.00	105.682(2)
β (deg)	91.561(2)	96.091(4)	90.00	102.272(2)
γ (deg)	90.00	90.00	90.00	90.00
V (Å^3)	2667.38(18)	2359.1(3)	8381.6(10)	1398.07(10)
Z	4	4	8	2
ρ_{calcd} (g cm^{-3})	1.199	1.606	1.249	1.497
μ (mm^{-1})	0.55	0.39	0.27	0.68
$\lambda_{MoK\alpha}$ (Å)	0.710 73	0.710 73	0.710 73	0.710 73
T (K)	173(2)	173(2)	173(2)	173(2)
measured reflns	31 467	19 529	19 101	30 997
indep reflns	6433	4093	5100	6090
reflns with $I > 2\sigma(I)$	4719	2620	4291	3646
R_{int}	0.038	0.035	0.056	0.073
F(000)	1024	1152	3328	640
R1 ($R[F^2 > 2\sigma(F^2)]$)	0.0492	0.0378	0.0525	0.0482
wR2 (F^2)	0.1344	0.0971	0.1386	0.0962
GOF	1.042	1.008	1.069	0.988
params	232	212	268	325
CCDC no.	957693	957694	957697	957701

Table 3. Crystallographic Details of Compounds 3Dipp, 3Ad, 16, and 14

	3Dipp[a]	3Ad	16	14
chem formula	$C_{24}H_{34}Cl_2N_2P_2$	$C_{20}H_{30}Cl_2N_2P_2$	$C_{38}H_{30}Cl_2N_2P_2$	$C_{21}H_{20}Cl_2NPSi$
fw (g mol^{-1})	483.37	431.30	647.48	416.34
color	colorless	colorless	colorless	colorless
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1$	$P2_1/c$	$P2_1/c$	$P2_1/n$
a (Å)	9.7403(3)	14.3494(7)	21.6043(3)	14.9031(4)
b (Å)	17.4140(6)	11.8705(6)	8.79950(10)	16.7323(4)
c (Å)	15.9047(5)	12.7844(7)	17.6203(3)	17.0281(4)
α (deg)	90.00	90.00	90.00	90.00
β (deg)	103.603(2)	110.751(3)	104.8450(10)	108.3870(10)
γ (deg)	90.00	90.00	90.00	90.00
V (Å^3)	2622.04(15)	2036.36(18)	3237.94(8)	4029.40(17)
Z	4	4	4	8
ρ_{calcd} (g cm^{-3})	1.224	1.407	1.328	1.373
μ (mm^{-1})	0.38	0.48	0.33	0.47
$\lambda_{MoK\alpha}$ (Å)	0.710 73	0.710 73	0.710 73	0.710 73
T (K)	173(2)	173(2)	200 (2)	173(2)
measured reflns	35 461	18 530	37 888	52 509
indep reflns	13525	4886	7385	10703
reflns with $I > 2\sigma(I)$	11 191	2891	5374	7976
R_{int}	0.029	0.070	0.106	0.046
F(000)	1024	912	1344	1728
R1 ($R[F^2 > 2\sigma(F^2)]$)	0.048	0.0497	0.0449	0.0469
wR2 (F^2)	0.1043	0.1093	0.1163	0.1198
GOF	1.048	0.938	1.019	1.037
params	558	235	397	643
CCDC no.	957698	957696	957699	957690

[a]A room temperature crystal structure of this compound was reported before by Burford et al. with similar unit cell parameters but the space group was $P2_1/c$ (see ref 10).

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Table 4. Selected Bond Lengths (Å) and Angles (deg)

P−N	P−E[b]	N−R	N−P−N	P−N−P	N−P−N−P	P···P
$[ClP(\mu\text{-}NN(SiMe_3)_2)]_2$ (**9**)						
1.704(2)	2.092(1)	1.427(3)	79.3(1)	99.0(1)	13.9(2)	2.596(1)
1.710(2)	2.092(1)	1.427(3)	79.3(1)	99.0(1)	10.8(2)	
$[R_fOP(\mu\text{-}NSiMe_3)]_2$ (**10**)						
1.702(1)	1.684(1)	1.763(1)	84.30(6)	95.70(6)	0.0	2.526(7)
1.705(1)	1.684(1)	1.763(1)	84.30(6)	95.70(6)	0.0	
$[ClP(\mu\text{-}NDipp)]_2$ (**3Dipp**)						
1.707(2)	2.0939(9)	1.435(3)	81.4(1)	97.7(1)	8.7(1)	2.572(9)
1.705(2)	2.0983(8)	1.439(3)	81.4(1)	97.9(1)	8.72(9)	
$[ClP(\mu\text{-}NDmp)]_2$[a](**3Dmp**)						
1.703(3)	2.111(1)	1.438(4)	81.6(1)	97.8(1)	8.1(1)	2.573(1)
1.700(2)	2.111(1)	1.431(4)	81.3(1)	98.2(1)	8.1(1)	
1.712(3)						
1.704(2)						
$[ClP(\mu\text{-}NAd)]_2$ (**3Ad**)						
1.697(2)	2.129(1)	1.477(3)	81.9(1)	98.2(1)	5.3(1)	2.562(9)
1.698(1)	2.129(1)	1.476(3)	81.8(1)	97.7(1)	5.3(1)	
1.701(2)						
1.701(2)						
$[ClP(\mu\text{-}NCPh_3)]_2$ (**16**)						
1.694(2)	2.117(8)	1.504(3)	81.02(8)	97.66(9)	8.79(9)	2.572(8)
1.701(2)	2.153(8)	1.499(2)	82.14(8)	97.82(9)	8.88(9)	
1.716(2)						
1.718(2)						
$[ClP(\mu\text{-}NPh)]_2$[a]						
1.698(1)	2.075(6)	1.423(9)	80.1(3)	99.7(4)	0	2.590(1)
1.691(1)	2.099(9)		80.5(4)	99.7(1)		
trans-$[ClP(\mu\text{-}NTer)]_2$ (*trans***15**)						
1.669(2)	2.099(2)	1.421(3)	82.3(1)	100.1(1)	−0.1(2)	2.604(1)
1.728(2)	2.085(2)	1.421(3)	80.3(1)	100.1(1)	0.1(2)	
1.729(2)						
1.740(2)						
$[Cl_2PN(Ph)P(\mu\text{-}NPh)]_2$ (**17**)						
1.710(2)	2.058(1)	1.409(3)	79.8(1)	100.3(1)	0	2.625(1)
1.711(2)	2.063(1)	1.409(3)	79.8(1)	100.3(1)		
1.734(2)						
1.680(2)						

[a]For $[ClP(\mu\text{-}NDmp)]_2$ and $[ClP(\mu\text{-}NPh)]_2$, values taken from refs 8b and 11a, respectively. [b]E = element attached to the P atom.

amino-substituted *trans-cyclo*-diphosphadiazane $[Cl_2PN(Ph)P(\mu\text{-}NPh)]_2$ shows a significant upfield shift (157 and 176 ppm for the exocyclic P atom) and a remarkably large $^2J(P-P)$ coupling constant of 483 Hz.

In the solid state for all considered species only the *cis* and for $[ClP(\mu\text{-}NTer)]_2$, $[R_fOP(\mu\text{-}NSiMe_3)]_2$ and $[Cl_2PN(Ph)P(\mu\text{-}NPh)]_2$ only the *trans* isomer could be detected as illustrated by X-ray studies (see below). As pointed out by Stahl,[4] most *cyclo*-diphosphazanes are thermodynamically more stable as the *cis* isomer while the *trans* isomer is the kinetically favored product.

X-ray Crystallography. The structures of compounds $[ClP(\mu\text{-}NR)]_2$ (R = Dipp, Ad, Ph_3C, $N(SiMe_3)_2$, Ter), $[Cl_2PN(Ph)P(\mu\text{-}NPh)]_2$, $[R_fOP(\mu\text{-}NSiMe_3)]_2$, and the starting materials Ph_3C-NH_2, $Ph_3C-N(H)PCl_2$, $Ph_3C-N(H)SiMe_3$, $Dipp-N(H)SiMe_3$, $Ter-N(SiMe_3)PCl_2$, and $Mes^*-N(SiMe_3)PCl_2$, along with those of the decomposition product **14** (Scheme 4), were determined. Tables 2 and 3 present the X-ray crystallographic data of the *cyclo*-diphosphadiazanes and compound **14**. Selected molecular parameters are listed in Table 4. The molecular structures of all other molecules are shown in the Supporting Information (Tables S3, S4, S5, and S6). X-ray quality crystals of all compounds were selected in Fomblin YR-1800 perfluoroether (Alfa Aesar) at ambient temperatures.

General Structural Trends. In all aminophosphane derivatives (see Supporting Information, Synthesis of Starting Material section), as expected, the central nitrogen atom is almost trigonal planar, and the phosphorus atom trigonal pyramidal coordinated. The sum of the bond angles at the amino nitrogen atom is always very close to 360° indicating a planar environment and hence a formal sp^2-hybridization. Therefore, the lone pair localized at this nitrogen atom is found in a p-type atomic orbital (AO). Small delocalization of this p-AO lone pair occurs, which is also known as hyperconjugation, leading to relatively short P−N bond lengths.[30] The P−N bond lengths of 1.64−1.68 Å are always slightly shorter than expected for a P−N single bond (cf. $\Sigma r_{cov}(N—P)$ = 1.82 Å, $\Sigma r_{cov}(N=P)$ = 1.62 Å).[27,28] The sum of the bond angles at the phosphorus atom are between 297° and 305°, in accord with structural data of known aminophosphane derivatives.[9,28]

cyclo-Diphosphadiazanes can exist as *cis* or *trans* isomers with the *cis* isomer being mostly the thermodynamically more stable

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isomer.[4] In general, the *cis* isomers have slightly puckered P_2N_2 rings with P−N−P−N dihedral angles between 5° and 14°,[1,4] whereas the rings in the *trans* isomers are planar as depicted in Figures 1−4. Both *trans* species $[Cl_2PN(Ph)P(\mu\text{-}NPh)]_2$ and

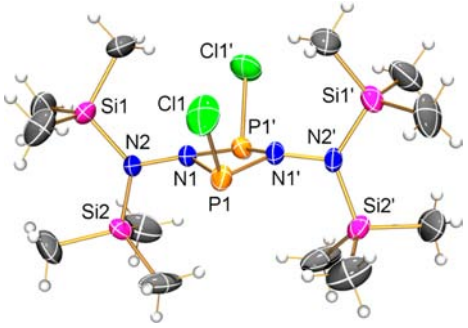

Figure 1. ORTEP drawing of the molecular structure $[ClP(\mu\text{-}NN(SiMe_3)_2)]_2$ (**9**) in the crystal. Thermal ellipsoids with 50% probability at 173 K. Only one independent molecule is shown.

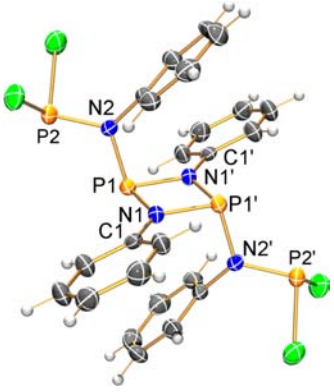

Figure 2. ORTEP drawing of the molecular structure of $[Cl_2PN(Ph)P(\mu\text{-}NPh)]_2$ (**17**) in the crystal. Thermal ellipsoids with 50% probability at 173 K.

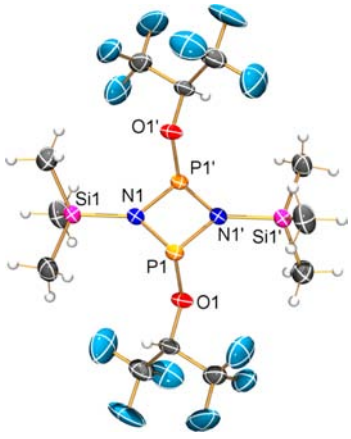

Figure 3. ORTEP drawing of the molecular structure of $[R_fOP(\mu\text{-}NSiMe_3)]_2$ (**10**) in the crystal. Thermal ellipsoids with 50% probability at 173 K.

$[R_fOP(\mu\text{-}NSiMe_3)]_2$ are centrosymmetric exhibiting a planar P_2N_2 four-membered heterocycle. On the contrary, *trans*-$[ClP(\mu\text{-}NTer)]_2$ is also planar but not centrosymmetric. P−N bond lengths between 1.67 and 1.74 Å (*cf.* 1.695(10) Å in $[ClP(\mu\text{-}NPh)]_2$)[11a] are observed in accord with structural data of known *cyclo*-diphosphadiazanes.[1,4,26] Comparison with the sum of the covalent radii (vide supra) and computations reveals highly polarized P−N bonds with bond orders (BO) between 1 and 2.[29]

The rather bulky groups used prevent all considered species from significant intermolecular interactions. Therefore, for instance, in the solid state structures of all considered compounds neither significant inter- nor intramolecular hydrogen bonding is observed. Only very weak CH···X and CH···P interactions are found between the $[XP(\mu\text{-}NR)]$ dimers (X = Cl, OR_f). Significant hydrogen bonding is known for smaller substituents.[23]

$[ClP(\mu\text{-}NN(SiMe_3)_2)]_2$ (**9**). This compound crystallizes from *n*-hexane in the monoclinic space group *P*2/*n* with four formula units per unit cell. Both independent molecules in the asymmetric unit possess almost identical structural parameters. The structure consists of well separated $[(Me_3Si)_2NNPCl]_2$ molecules with no significant intermolecular contacts.

The molecule adopts a staggered configuration (Figure 1) with the two planes P1−N1−P1′−N2 and N1−N2−Si1−Si2 perpendicular to each other (∠P1−N1−N2−Si1 = 98.5°). The phosphorus atom sits in a strongly distorted tetrahedral environment with bond angles between 79° and 107°. The experimentally determined P−N bond lengths of 1.704(2) and 1.710(2) Å are slightly shorter than expected for a typical P−N single bond[28,30,31] but comparable with the 1.707(3) Å in the 1,2,3-trisphosphabicyclo[1.1.0] butane species $[(Me_3Si)_2NN(SiMe_3)P-P-P-C(SiMe_3)_2]$.[32] To get insight into the bonding along the PN units, computations at the B3LYP/6-31G(d) level of theory were carried out (see Supporting Information). According to NBO analysis,[33] the σ bond system along the P1−N1−N2 unit is highly polarized between P1 and N2 and almost ideally covalent between the adjacent N1−N2 single bond with a bond distance of 1.427(3) Å (*cf.* 1.473(4) Å in $PhP(Cl)N(SiMe_3)N(SiMe_3)_2$,[30] Table 4). The calculated NBO partial charges are Q_{P1} = +1.22 on phosphorus, Q_{N1} = −0.94 on the adjacent nitrogen, and Q_{N2} = −1.14 *e* on the second nitrogen atom.

$[Cl_2PN(Ph)P(\mu\text{-}NPh)]_2$ (**17**). This compound was obtained in the reaction of *N*-trimethylsilylaniline, $Ph-N(SiMe_3)H$, with PCl_3 after addition of *n*-BuLi at ambient temperature. Recrystallization from CH_2Cl_2 resulted in the deposition of colorless crystals of **17** at −5 °C. $[Cl_2PN(Ph)P(\mu\text{-}NPh)]_2$ crystallizes in the triclinic space group $P\bar{1}$ with two independent molecules per unit cell. No significant intermolecular contacts are observed. The asymmetric unit consists of two Ph−N−P−N(Ph)−PCl_2 fragments. All four phenyl rings of one molecule are arranged parallel to each other. The phosphorus atom sits in a trigonal pyramidal environment in the planar P_2N_2 ring with the two $N(Ph)PCl_2$ groups in *trans* position (Figure 2). The phenyl group attached to the endocyclic N atoms is slightly twisted with respect to the P_2N_2 plane (25.9°). The P−N bond lengths within the P_2N_2 ring are almost identical with 1.710(2) and 1.711(2) Å, which are slightly shorter compared to the exocyclic P1−N2 distance of 1.734(2), but longer than the N2−P2 bond length with 1.680(2) Å. Both the ring nitrogen and the exocyclic nitrogen atoms are almost planar coordinated. Therefore, the lone pair localized at these nitrogen atoms is located in a p-atomic orbital which undergoes hyperconjugation with acceptor orbitals of adjacent groups, *e.g.*, the PCl_2 fragment.

$[R_fOP(\mu\text{-}NSiMe_3)]_2$ (**10**). This compound crystallizes solvent free in the monoclinic space group *C*2/*c* with four formula units

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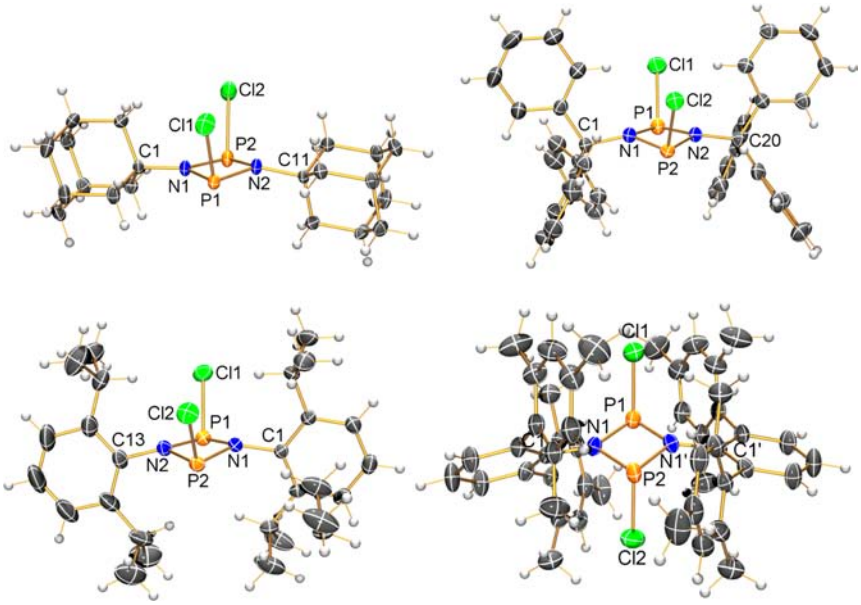

Figure 4. ORTEP drawings of the molecular structure of $[ClP(\mu\text{-}NR)]_2$ in the crystal [top left, R = Ad (**3**Ad); top right, R = Ph_3C (**16**); bottom left, R = Dipp (**3**Dipp); bottom right, R = Ter (*trans***15**)]. Thermal ellipsoids with 50% probability at 173 K.

per unit cell. No significant intermolecular contacts are observed. The asymmetric unit consists of a half molecule, which lies on a 2-fold crystallographic axis with the whole molecule generated by the symmetry operation $x + {}^1/_2$, $-y + {}^1/_2$, $-z$ as depicted in Figure 3 leading to a centrosymmetric dimer.

The $CH(CF_3)_2$ group is disordered and split into two parts. Compound **10** adopts the *trans* configuration with respect to the perfluorinated alkoxy group. Thus, the P_2N_2 ring in **10** is planar with two very similar PN bond lengths [1.702(1) and 1.705(1) Å]. The N1−P−N1′ angle with 84.30(6)° is significantly smaller compared to the P1−N1−P1′ [95.70(6)°] angle. The N−P−O angles are found between 97.6° and 103.7°.

$[ClP(\mu\text{-}NR)]_2$ (R = Ad, Ph_3C, Dipp, and Ter). While compounds $[ClP(\mu\text{-}NR)]_2$ (R = Ad, Ph_3C) and $[ClP(\mu\text{-}NDipp)]_2$ crystallize in the monoclinic space groups $P2_1/c$ and $P2_1$, respectively, with four molecules per unit cell, for $[ClP(\mu\text{-}NTer)]_2$ the orthorhombic space group *Fdd*2 was found with eight molecules in the unit cell. $[ClP(\mu\text{-}NCPh_3)]_2$ crystallizes from CH_2Cl_2 in the monoclinic space group $P2_1$ with two (disordered) solvent molecules per unit cell. In contrast to $[ClP(\mu\text{-}NTer)]_2$, which crystallizes as *trans* isomer, the molecular structures of all dichloro-substituted compounds $[ClP(\mu\text{-}NR)]$ (Figure 4) display *cis*-substituted dimers with respect to the position of the chlorine atoms and a slightly puckered P_2N_2 core (Table 4) protected by two bulky organic groups. No significant intermolecular contacts are observed between $[ClP(\mu\text{-}NR)]_2$ molecules. It is interesting to note that *cis*-$[ClP(\mu\text{-}NTer)]_2$ crystallizes in the monoclinic space group $C2/c$ with four formula units per unit cell. The asymmetric unit consists of a half molecule, which lies on a 2-fold crystallographic axis.[26]

Astonishingly, the metrical parameters of the P_2N_2 core such as the P···P and P−N distances or the N−P−N and P−N−P angles (Table 4) do not change significantly along the $[ClP(\mu\text{-}NR)]_2$ (R = Ad, Ph_3C, Dipp, and Ter), and are in the same range found for the *cis*-$[ClP(\mu\text{-}NN(SiMe_3)_2)]_2$ and *trans*-$[R_fOP(\mu\text{-}NSiMe_3)]_2$ species. Always two slightly different P−N bond lengths are found. The P···P distances between 2.57 and 2.62 Å are only slightly longer than the sum of the covalent radii (2.20 Å) but significantly shorter than the sum of the van der Waals radii (3.8 Å).[31] Thus (like for all other *cyclo*-diphosphadiazanes),[1] strong van der Waals interactions across the ring can be assumed. Similar structural features are found in $[XE(\mu\text{-}NR)]_2$ (E = P, As, Sb, and Bi; X = halogen, pseudohalogen)[4,6,34] and the biradicaloids $[E(\mu\text{-}NR)]_2$ (E = P, As; R = Ter, Hyp).[35]

cyclo-Silazane ***14.*** This compound crystallizes in the orthorhombic space group $P2_1/n$ with eight formula units per unit cell (see Figure 5). No significant intermolecular contacts are observed. The asymmetric unit consists of two disordered independent molecules. The C_3SiN heterocycle is almost planar with dihedral angles between 3.2° and 16.8°, and also the deviation from planarity for the bicycle is rather small (3.9°). The angle sum around the N atom is close to 360° (359.9°) displaying a planar environment around the nitrogen with a

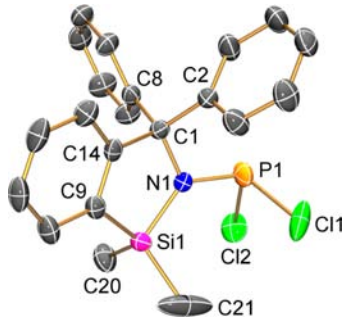

Figure 5. ORTEP drawing of the molecular structure of **14** in the crystal. Thermal ellipsoids with 50% probability at 173 K. Aryl hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): N1−C1 1.512(2), N1−P1 1.656(2), N1−Si1 1.769(2), P1−Cl2 2.0695(9), P1−Cl1 2.090(2); C1−N1−P1 114.9(1), C1−N1−Si1 114.2(1), P1−N1−Si1 130.8(1), N1−P1−Cl2 100.30(7), N1−P1−Cl1 104.3(8), Cl2−P1−Cl1 97.03(5), N1−Si1−C9 91.3(9), N1−Si1−C20 113.1(1), N1−C1−C14 104.9(2).

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nitrogen lone pair localized in a p-atomic orbital (AO). NBO analysis indicates strong intramolecular interactions of the p-AO lone pair with the antibonding σ^*(P−Cl) bonds which strengthens the P−N bond but weakens the P−Cl bonds. Therefore, the experimentally determined P1−N1 bond length of N1−P1 with 1.656(2) Å is significantly shorter than expected for a typical P−N single bond[27] indicating a strong hyperconjugation interaction (*cf.* 1.704(1) and 1.703(1) Å in *p*-$C_6H_4[N(PCl_2)_2]_2$).[36] Typical single bonds are found for the Si−N (1.769(2), *cf.* Σr_{cov} = 1.87 Å)[27] and the C−N bonds (1.512(2) Å, Σr_{cov} = 1.46 Å).[27] The phosphorus atom sits in trigonal pyramidal environment with a Cl−P−Cl angle of 97.03(5)° and a N−P−Cl angle of 104.3(8)°.[30] The C1−N1−Si1 angle with 114.2(1)° is rather large compared to the small C9−Si−N1 angle (91.3(9)°).

CONCLUSION

Usually, synthesis of *cyclo*-diphosphadiazanes is achieved by treatment of primary amines and ECl_3 (E = P and As) with bases such as Et_3N, *n*-BuLi, DBU, or LDA. Depending on the used base and reaction conditions different product mixtures are obtained, which often are difficult to be separated. Therefore, a convenient synthetic route using trimethylsilyl-substituted amino(dichloro)phosphanes, $R-N(SiMe_3)PCl_2$, was utilized to form *cyclo*-diphosph(III)azanes in a one-pot-reaction. By this method, electron-rich/-poor aryl-, silyl-, and bissilylamino-substituted *cyclo*-diphosphazanes are accessible upon thermal Me_3SiCl elimination. The unprecedented $(Me_3Si)_2N$-substituted species $[ClP(\mu\text{-}NN(SiMe_3)_2)]_2$ was isolated simply by adding a mixture of R_fOH/base to tris(trimethylsilyl)hydrazine-(dichloro)phosphane, $(Me_3Si)_2N-(Me_3Si)N-PCl_2$ (Scheme 4). Additionally, the difficulties with the preparation of *cyclo*-diphosphadiazanes depending on the starting materials, solvents, and bases due to the competition of different reaction channels are discussed. For example, there are two competing reaction channels for $R-N(SiMe_3)PCl_2$, which might be caused by steric or electronic features of the ligand.

EXPERIMENTAL SECTION

General Information. All manipulations were carried out under oxygen- and moisture-free conditions under argon using standard Schlenk or drybox techniques.

Dichloromethane, CH_2Cl_2, was purified according to a literature procedure,[37] dried over P_4O_{10}, and freshly distilled prior to use. Toluene, diethylether, and THF were dried over Na/benzophenone and freshly distilled prior to use; *n*-hexane was dried over Na/benzophenone/tetraglyme and freshly distilled prior to use. 2,6-Diisopropylphenylamine Dipp−NH_2 (Merck), 2,6-dimethylphenylamine Dmp−NH_2 (Arcos), *p*-toluenesulfonylamine *p*-Tosyl−NH_2 (gift of Professor H. Reinke, University of Rostock), adamantylamine Ad−NH_2 (ABCR), and *n*-BuLi (2.5 M, Acros) were used as received. PCl_3 (99%, Acros), Me_3SiCl (Sigma-Aldrich), 1,8-diazabicyclo[5.4.0]-undec-7-ene DBU (ABCR), 1,1,1,3,3,3-hexafluoroisopropanole R_fOH (Sigma-Aldrich), NEt_3 (Merck), *n*-octyl−NH_2 (gift of Professor H. Reinke, University of Rostock), and aniline (Sigma-Aldrich) were freshly distilled prior to use. *N,N′,N′*-Tris(trimethlysilyl)hydrazine-(dichloro)phosphane $(Me_3Si)_2N-N(SiMe_3)PCl_2$,[17] *N*-tris-(trimethylsilyl)silyl-*N*-trimethylsilylamino(dichloro)phosphane $(Me_3Si)_3Si-N(SiMe_3)PCl_2$,[15] *N,N*-bis(trimethylsilyl)amino(dichloro)-phosphan $(Me_3Si)_2NPCl_2$,[22] *N*-(2,4,6-tri-*tert*-butylphenyl)-*N*-trimethylsilyl-amine Mes*−$N(SiMe_3)H$,[38] *N*-triphenylmethylamine Ph_3C-NH_2,[39] and 2,6-bis-(2,4,6-trimethylphenyl)phenyl-*N*-trimethylsilyl-amine Ter−$N(SiMe_3)H$[40] have been reported previously and were prepared according to literature procedures.

NMR. $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, ^{29}Si-INEPT, $^{19}F\{^1H\}$, and ^1H NMR spectra were recorded on Bruker spectrometers AVANCE 300 and AVANCE 500, respectively. The ^1H and ^{13}C chemical shifts were referenced to solvent signals (C_6D_6, δ ^1H = 7.15, δ ^{13}C = 128.0; CD_2Cl_2, δ ^1H = 5.31, δ ^{13}C = 54.0). The ^1H and ^{13}C NMR signals were assigned by DEPT and two-dimensional correlation spectra (HSQC and HMBC) using standard pulse sequences (standard Bruker software). The ^{19}F, ^{29}Si, and ^{31}P chemical shifts are referred to $CFCl_3$, TMS, and H_3PO_4 (85%), respectively. CD_2Cl_2 was dried over P_4O_{10}, and C_6D_6 was dried over Na/benzophenone.

IR. Nicolet 380 FT-IR with a Smart Orbit ATR device was used.

Raman. Bruker VERTEX 70 FT-IR with RAM II FT-Raman module, equipped with a Nd:YAG laser (1064 nm), was used.

CHN Analyses. Analysator Flash EA 1112 from Thermo Quest, or C/H/N/S-Mikroanalysator TruSpec-932 from Leco, was used.

Melting Points. These are uncorrected (EZ-Melt, Stanford Research Systems). Heating rate is 20 °C/min (clearing points are reported).

DSC. DSC 823e from Mettler-Toledo (Heating-rate 5 °C/min) was used.

MS. Finnigan MAT 95-XP from Thermo Electron was used.

X-ray Structure Determination. X-ray quality crystals of all compounds were selected in Fomblin YR-1800 perfluoroether (Alfa Aesar) at ambient temperatures. The samples were cooled to 173(2) K during measurement. The data were collected on a Bruker Apex Kappa-II CCD diffractometer or on a Bruker-Nonius Apex X8 CCD diffractometer using graphite monochromated Mo Kα radiation (λ = 0.710 73 Å). The structures were solved by direct methods (*SHELXS-97*)[41] and refined by full-matrix least-squares procedures (*SHELXL-97*).[42] Semiempirical absorption corrections were applied (*SADABS*).[43] All non-hydrogen atoms were refined anisotropically; hydrogen atoms (except from H atoms connected to N atoms) were included in the refinement at calculated positions using a riding model.

Syntheses. *$[ClP(\mu\text{-}NN(SiMe_3)_2)]_2$ (**9**).* To a stirred solution of *N,N′,N′*-tris(trimethylsilyl)hydrazine(dichloro)phosphane $(Me_3Si)_2N-N(SiMe_3)PCl_2$ (1.398 g, 4.00 mmol) in THF (10 mL) was added hexafluoroisopropanole (R_fOH) (0.672 g, 4.00 mmol) in THF (10 mL) dropwise at −60 °C over a period of 10 min. To the resulting colorless solution was added DBU (0.639 g, 4.20 mmol) dropwise at −55 °C. The resulting yellowish suspension was warmed to ambient temperature and stirred for 2 h. The solvent was removed *in vacuo*, resulting in a yellowish residue which was extracted with *n*-hexane (10 mL) and filtered (and washed several times by repeated backdistillation of solvent). The resulting yellow solution was concentrated *in vacuo* to incipient crystallization and stored for 1 h at 5 °C, resulting in the deposition of colorless crystals. Removal of supernatant by syringe and drying *in vacuo* yielded 0.684 g (2.840 mmol, 71%) of **9** as colorless crystals. Mp: 140 °C. Anal. Calcd % (Found) for $C_{12}H_{36}Cl_2N_4P_2Si_4$ (481.64): C 29.92 (30.72), H 7.53 (7.35), N 11.63 (11.37). NMR (ratio *cis*:*trans* = 87:13) for *cis* follow. ^1H NMR (25 °C, CD_2Cl_2, 300.13 MHz): δ = 0.25 (s, 36H, $N(Si(CH_3)_3)_2$). $^{13}C\{^1H\}$ NMR (25 °C, CD_2Cl_2, 75.5 MHz):δ = 2.2 (s, $Si(CH_3)_3$), 2.6 (t, $^4J(^{13}C-^{31}P)$ = 3.0 Hz, $Si(CH_3)_3$). ^{29}Si NMR (25 °C, CD_2Cl_2, 59.6 MHz): δ = 13.1, 12.5. $^{31}P\{^1H\}$ NMR (25 °C, CD_2Cl_2, 121.5 MHz): δ = 212.4. NMR data for *trans* follow. ^1H NMR (25 °C, CD_2Cl_2, 300.13 MHz): δ = 0.30 (s, 36H, $N(Si(CH_3)_3)_2$). $^{13}C\{^1H\}$ NMR (25 °C, CD_2Cl_2, 75.5 MHz): δ = 3.2 (s, $Si(CH_3)_3$). ^{29}Si NMR (25 °C, CD_2Cl_2, 59.6 MHz): δ = 13.6. $^{31}P\{^1H\}$ NMR (25 °C, CD_2Cl_2, 121.5 MHz): δ = 308.4. IR (ATR, 25 °C, 32 scans, cm^{-1}): 2954 (m), 2898 (m), 1936 (w), 1873 (w), 1575 (m), 1434 (w), 1404 (m), 1373 (w), 1291 (m), 1251 (s), 1195 (m), 1116 (m), 1056 (w), 1009 (w), 927 (m), 887 (m), 835 (w), 818 (m), 771 (m), 754 (m), 684 (w), 671 (s), 623 (s). Raman (800 mW, 839 scans, 25 °C, cm^{-1}): 2959 (5), 2901 (10), 1410 (2), 1266 (1), 1250 (1), 1210 (1), 963 (1), 920 (1), 856 (1), 837 (1), 749 (1), 752 (1), 686 (2), 639 (4), 576 (6), 490 (2), 413 (2), 370 (2), 343 (3), 279 (2), 263 (2), 238 (3), 224 (3), 190 (3), 145 (2), 96 (4). MS (CI^+, isobutane): 205 $[(Me_3Si)_2NP]^+$, 240 $[^1/_2M]^+$, 445 $[M - Cl]^+$, 481 $[M + H]^+$.

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Crystals suitable for X-ray crystallographic analysis were obtained by cooling of a saturated *n*-hexane solution of **9** to 5 °C.

*[R_fOP(μ-NSiMe$_3$)]$_2$ (**10**).* To a stirred solution of *N*-tris-(trimethylsilyl)silyl-*N*-trimethylsilylamino(dichloro)phosphane $(Me_3Si)_3Si-N(SiMe_3)PCl_2$ (0.437 g, 1.00 mmol) in THF (10 mL) was added DBU (0.160 g, 1.05 mmol) dropwise at −70 °C over a period of 15 min. To the resulting colorless suspension was added hexafluoroisopropanole R_fOH (0.168 g, 1.00 mmol) in THF (5 mL) dropwise at −65 °C. The yellowish suspension was stirred for 1 h at low temperature (−65 to −30 °C), warmed to ambient temperature, and stirred for another 2 h. The solvent was removed *in vacuo*, resulting in a yellowish residue which was extracted with *n*-hexane (10 mL). After filtration (F4), the yellow solution was concentrated *in vacuo* to incipient crystallization and stored at −80 °C for 12 h, resulting in the deposition of colorless crystals. Removal of supernatant by syringe and drying *in vacuo* yielded 0.176 g (0.674 mmol, 67%) of **10** as colorless crystals [only stable at low temperature (−80 °C)]. NMR (ratio *cis*:*trans* = 46:54, at temperatures below −50 °C only the *cis* isomer was observed (173.7 ppm); at ambient temperature a *cis*−*trans* conversion occurs slowly) data for *cis* follow. ^{1}H NMR (25 °C, CD_2Cl_2, 300.13 MHz): δ = 0.22 (s, 18H, Si(CH_3)$_3$), 5.19 (m, 2H, $^3J(^1H-^{19}F)$ = 5.2 Hz, C*H*). $^{13}C\{^1H\}$ NMR (25 °C, CD_2Cl_2, 75.5 MHz): δ = 0.2 (t, $^3J(^{13}C-^{31}P)$ = 4.3 Hz, Si(CH_3)$_3$), 67.9−70.8 (m, $^2J(^{13}C-^{31}P)$ = 2.9 Hz, $^2J(^{13}C-^{19}F)$ = 34.0 Hz, *C*H), 121.7 (q, $^1J(^{13}C-^{19}F)$ = 283.0 Hz, CF_3). $^{19}F\{^1H\}$ NMR (25 °C, CD_2Cl_2, 282.4 MHz): δ = −73.9 (m, 12F, CF_3). ^{29}Si NMR (25 °C, CD_2Cl_2, 59.6 MHz): δ = 8.7. $^{31}P\{^1H\}$ NMR (25 °C, CD_2Cl_2, 121.5 MHz): δ = 173.7. Data for *trans* follow. ^{1}H NMR (25 °C, CD_2Cl_2, 300.13 MHz): δ = 0.14 (s, 18H, Si(CH_3)$_3$), 4.79 (m, 2H, $^3J(^1H-^{19}F)$ = 6.0 Hz, $^3J(^1H-^{31}P)$ = 8.5 Hz, C*H*). $^{13}C\{^1H\}$ NMR (25 °C, CD_2Cl_2, 75.5 MHz): δ = −0.1 (m, Si(CH_3)$_3$). $^{19}F\{^1H\}$ NMR (25 °C, CD_2Cl_2, 282.4 MHz): δ = −73.1 (m, 12F, CF_3). ^{29}Si NMR (25 °C, CD_2Cl_2, 59.6 MHz): δ = 7.2. $^{31}P\{^1H\}$ NMR (25 °C, CD_2Cl_2, 121.5 MHz): δ = 264.9.

Crystals suitable for X-ray crystallographic analysis were obtained by slow cooling of a saturated *n*-hexane solution of **10** to −80 °C.

*[ClP(μ-NDipp)]$_2$ (**3Dipp**).* To a stirred solution of *N*-(2,6-diisopropylphenyl)-*N*-trimethylsilylamine, Dipp−N(SiMe$_3$)H (0.499 g, 2.00 mmol), in Et_2O (15 mL) was added *n*-BuLi (2.5M, 0.84 mL, 2.1 mmol) dropwise at ambient temperature over a period of 10 min. The resulting pale yellow solution was added dropwise to a solution of PCl_3 (0.302 g, 2.20 mmol) in Et_2O (5 mL) at −30 °C over a period of 20 min. The resulting yellow suspension was warmed to ambient temperature and stirred for 1 h. The solvent was removed *in vacuo*, resulting in a yellowish residue which was extracted with *n*-hexane (10 mL) After filtration (F4) the resulting pale yellow solution was concentrated to incipient crystallization *in vacuo* and stored at −40 °C, resulting in the deposition of colorless crystals. Removal of supernatant by syringe and drying *in vacuo* yielded 0.401 g (1.66 mmol, 83%) of **3**Dipp as colorless crystals. Mp: 216 °C. Anal. Calcd % (Found) for $C_{24}H_{34}Cl_2N_2P_2$ (483.39): C 59.63 (58.70), H 7.09 (7.39), N 5.80 (5.70). NMR (ratio *cis*:*trans* = 99:1) data for *cis* follow. ^{1}H NMR (25 °C, CD_2Cl_2, 300.13 MHz): δ = 1.32 (d, 24H, $^3J(^1H-^1H)$, = 6.8 Hz, CH_3), 3.88 (s, 4H, C*H*), 7.15−7.40 (m, 6H, Ph). $^{13}C\{^1H\}$ NMR (25 °C, CD_2Cl_2, 75.5 MHz): δ = 25.6 (s, CH_3), 124.8 (s, *m*-Ph), 129.1 (s, *p*-Ph), 131.0 (t, $^2J(^{13}C-^{31}P)$ = 7.15 Hz, C_q), 149.6 (m, C_q). $^{31}P\{^1H\}$ NMR (25 °C, CD_2Cl_2, 121.5 MHz): δ = 210.5 (*cis*), 291.5 (*trans*). IR (ATR, 25 °C, 32 scans, cm^{-1}): 3060 (w), 3015 (w), 2957 (s), 2923 (m), 2864 (m), 1586 (w), 1519 (w), 1463 (m), 1455 (w), 1442 (s), 1383 (s), 1362 (s), 1346 (w), 1319 (m), 1300 (w), 1280 (w), 1248 (s), 1197 (s), 1180 (m), 1163 (w), 1148 (w), 1103 (s), 1055 (m), 1039 (m), 974 (w), 953 (w), 934 (w), 922 (m), 903 (s), 799 (s), 747 (w), 738 (w), 722 (m), 668 (w), 632 (w), 617 (w), 600 (m), 573 (w), 536 (s), 528 (s). Raman (600 mW, 250 scans, 25 °C, cm^{-1}): 3169 (1), 3088 (2), 3061 (3), 3028 (2), 3017 (2), 2965 (7), 2951 (6), 2932 (9), 2909 (8), 2866 (7), 2757 (2), 2714 (2), 2610 (1), 2519 (1), 1590 (6), 1462 (4), 1443 (4), 1385 (1), 1362 (1), 1339 (3), 1316 (2), 1299 (2), 1281 (10), 1225 (2), 1198 (1), 1181 (2), 1164 (2), 1108 (3), 1048 (2), 982 (2), 955 (2), 924 (1), 888 (3), 840 (1), 793 (1), 733 (1), 678 (1), 633 (4), 602 (1), 573 (1), 539 (2), 496 (2), 448 (2), 421 (4), 381 (1), 340 (2), 290 (3), 246 (3), 174 (4), 132 (4), 103 (5), 84 (9). MS (CI$^+$, isobutane): 206 [DippNP]$^+$, 241 [$^1/_2$M]$^+$, 447 [M − Cl]$^+$, 483 [M + H]$^+$.

Crystals suitable for X-ray crystallographic analysis were obtained by slow cooling of a saturated *n*-hexane solution of **3**Dipp to −40 °C.

*[ClP(μ-NDmp)]$_2$ (**3Dmp**).* To a stirred solution of *N*-(2,6-dimethylphenyl)-*N*-trimethylsilylamine, Dmp−N(SiMe$_3$)H (0.387 g, 2.00 mmol), in Et_2O (10 mL) was added *n*-BuLi (2.5M, 0.84 mL, 2.1 mmol) dropwise at ambient temperature over a period of 10 min. The resulting pale yellow solution was added dropwise to a solution of PCl_3 (0.302 g, 2.20 mmol) in Et_2O (5 mL) at −30 °C over a period of 20 min. The resulting colorless suspension was warmed to ambient temperature and stirred for 1 h. The solvent was removed *in vacuo*, resulting in a colorless residue which was extracted with *n*-hexane (10 mL) After filtration (F4) the resulting pale yellow solution was concentrated *in vacuo* to incipient crystallization and stored at −40 °C, resulting in the deposition of colorless crystals. Removal of supernatant by syringe and drying *in vacuo* yielded 0.318 g (1.71 mmol, 86%) of **3**Dmp as colorless crystals. Mp: 115 °C. Anal. Calcd % (Found) for $C_{16}H_{18}Cl_2N_2P_2$: C 51.77 (51.88), H 4.89 (5.83), N 7.55 (7.08). NMR (ratio *cis*:*trans* = 93:7) data for *cis* follow. ^{1}H NMR (25 °C, CD_2Cl_2, 300.13 MHz): δ = 2.68 (s, 12H, CH_3), 7.14 (m, 6H, Ph). $^{13}C\{^1H\}$ NMR (25 °C, CD_2Cl_2, 75.5 MHz): δ = 19.8 (t, $^4J(^{13}C-^{31}P)$ = 3.2 Hz, CH_3), 128.8 (s, Ph), 129.5 (s, Ph), 129.8 (s, Ph). $^{31}P\{^1H\}$ NMR (25 °C, CD_2Cl_2, 121.5 MHz): δ = 210.4 (*cis*), 295.6 (*trans*). IR (ATR, 25 °C, 32 scans, cm^{-1}): 3063 (w), 3020 (w), 2973 (w), 2963 (w), 2946 (w), 2917 (w), 2851 (w), 2729 (w), 2683 (w), 2584 (w), 2567 (w), 1585 (w), 1574 (w), 1532 (w), 1520 (w), 1469 (s), 1442 (m), 1378 (m), 1289 (w), 1261 (s), 1205 (s), 1167 (m), 1097 (m), 1057 (w), 1032 (w), 985 (w), 973 (w), 942 (w), 918 (m), 892 (s), 774 (s), 740 (m), 720 (m), 665 (w), 615 (w), 580 (m), 560 (m), 540 (w), 532 (s). Raman (1000 mW, 250 scans, 25 °C, cm^{-1}): 3175 (1), 3067 (2), 3038 (2), 2974 (1), 2920 (4), 2865 (1), 2731 (1), 2568 (1), 1474 (2). 1445 (1), 1430 (1), 1383 (2), 1329 (1), 1289 (7), 1229 (1), 1206 (1), 1169 (1), 1106 (2), 1029 (1), 990 (1), 976 (1), 921 (1), 826 (1), 776 (1), 751 (1), 708 (1), 664 (1), 616 (5), 564 (2), 543 (2), 514 (1), 502 (1), 491 (1), 462 (2), 400 (1), 371 (3), 348 (1), 330 (1), 317 (1), 280 (1), 224 (3), 215 (3), 195 (2), 132 (2), 89 (10). MS (CI$^+$, isobutane): 150 [$^1/_2$M − Cl]$^+$, 185 [$^1/_2$M]$^+$, 335 [M − Cl]$^+$, 371 [M + H]$^+$.

*[ClP(μ-NAd)]$_2$ (**3Ad**).* To a stirred solution of *N*-adamantyl-*N*-trimethylsilylamine, Ad−N(SiMe$_3$)H (0.989 g, 4.43 mmol), in Et_2O (10 mL) was added *n*-BuLi (2.5M, 1.90 mL, 4.65 mmol) dropwise at ambient temperature over a period of 10 min. The resulting pale yellow solution was added dropwise to a solution of PCl_3 (1.830 g, 13.30 mmol) in Et_2O (5 mL) at −30 °C over a period of 20 min. The resulting pale yellow suspension was warmed to ambient temperature and stirred for 1 h. The solvent was removed *in vacuo*, resulting in a pale yellow residue which was extracted with *n*-hexane (10 mL) After filtration (F4) the resulting champagne colored solution was concentrated *in vacuo* to incipient crystallization and stored at ambient temperature, resulting in deposition of colorless crystals. Removal of supernatant by syringe and drying *in vacuo* yielded 0.728 g (3.38 mmol, 76%) of **3**Ad as colorless crystals. Mp: 263 °C (dec). Anal. Calcd % (Found) for $C_{20}H_{30}Cl_2N_2P_2$ (431.32): C 55.69 (54.78), H 7.01 (7.30), N 6.49 (6.41). NMR (ratio *cis*:*trans* = 100:0) data for *cis* follow. ^{1}H NMR (25 °C, CD_2Cl_2, 300.13 MHz): δ = 1.66 (m, 12H, CH_2), 1.83−2.04 (m, 12H, CH_2), 2.12 (m, 6H, C*H*). $^{13}C\{^1H\}$ NMR (25 °C, CD_2Cl_2, 75.5 MHz): δ = 30.0 (s, CH), 36.1 (s, CH_2), 43.9 (t, $^3J(^{13}C-^{31}P)$ = 6.1 Hz, CH_2). $^{31}P\{^1H\}$ NMR (25 °C, CD_2Cl_2, 121.5 MHz): δ = 206.0. IR (ATR, 25 °C, 32 scans, cm^{-1}): 2904 (s), 2847 (m), 2682 (w), 2634 (w), 2593 (w), 2361 (w), 2343 (w), 2329 (w), 1646 (m), 1594 (w), 1515 (w), 1473 (w), 1447 (m), 1366 (m), 1354 (m), 1346 (w), 1305 (m), 1283 (m), 1262 (w), 1231 (m), 1186 (m), 1156 (w), 1132 (s), 1118 (w), 1101 (w), 1094 (m), 1075 (m), 1043 (m), 1008 (m), 990 (m), 959 (w), 947 (s), 889 (s), 867 (m), 815 (w), 804 (m), 788 (m), 760 (m), 730 (w), 686 (m), 643 (w), 601 (w), 583 (w), 559 (w), 551 (w), 538 (w), 527 (w). Raman (400 mW, 200 scans, 25 °C, cm^{-1}): 2922 (10), 2884 (5), 2855 (4), 2726 (1), 2710 (1), 2685 (1), 2633 (1), 1435 (3), 1368 (1), 1349 (1), 1314 (1), 1275 (2),

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1266 (2), 1233 (1), 1191 (4), 1167 (1), 1100 (2), 1044 (1), 1032 (1), 1000 (1), 984 (2), 971 (3), 944 (1), 884 (1), 867 (1), 820 (1), 766 (5), 722 (1), 687 (3), 645 (1), 610 (1), 585 (2), 492 (1), 464 (1), 452 (1), 423 (1), 396 (3), 375 (1), 340 (1), 315 (2), 298 (1), 288 (1), 263 (2), 205 (2), 194 (3), 176 (2), 151 (2), 103 (2). MS (CI^+, isobutane): 395 $[M - Cl]^+$, 430 $[M]^+$.

Crystals suitable for X-ray crystallographic analysis were obtained from the above solution of **3**Ad at ambient temperature.

*$[ClP(\mu\text{-}NCPh_3)]_2$ (**16**).* To a stirred solution of *N*-(triphenylmethyl)-amino(dichloro)phosphane, $Ph_3C-N(H)PCl_2$ (0.720 g, 2.00 mmol), in Et_2O (20 mL) was added NEt_3 (0.223 g, 2.20 mmol) dropwise at −60 °C. The resulting colorless suspension was warmed to ambient temperature and stirred for 1 h. The solvent was removed *in vacuo*, and the yellowish residue was extracted with toluene (15 mL). After filtration (F4) the solvent was removed *in vacuo*, and CH_2Cl_2 (2 mL) was added. The champagne colored solution was concentrated *in vacuo* to incipient crystallization and stored at −20 °C, resulting in the deposition of colorless crystals. Removal of supernatant by syringe and drying *in vacuo* yielded 0.517 g (1.60 mmol, 80%) of **16** as colorless crystals. Mp: 248 °C (dec). Anal. Calcd % (Found) for $C_{38}H_{30}Cl_2N_2P_2$ (647.51): C 70.49 (69.91), H 4.67 (4.58), N 4.33 (4.30). NMR (ratio *cis*:*trans* = 100:0) data for *cis* follow. ^1H NMR (25 °C, CD_2Cl_2, 300.13 MHz): δ = 6.60−7.67 (m, 30H, Ph). $^{13}C\{^1H\}$ NMR (25 °C, CD_2Cl_2, 75.5 MHz): δ = 76.8 (t, $^2J(^{13}C-^{31}P)$ = 10.5 Hz, C_q), 128.4 (s, Ph), 128.6 (s, Ph), 130.5 (t, $^4J(^{13}C-^{31}P)$ = 2.7 Hz, *o*-Ph), 143.1 (t, $^3J(^{13}C-^{31}P)$ = 2.9 Hz, *i*-Ph). $^{31}P\{^1H\}$ NMR (25 °C, CD_2Cl_2, 121.5 MHz): δ = 197.6. IR (ATR, 25 °C, 32 scans, cm^{-1}): 3079 (w), 3056 (w), 3023 (w), 3004 (w), 1595 (w), 1490 (m), 1445 (m), 1321 (w), 1285 (w), 1267 (m), 1212 (m), 1184 (w), 1152 (m), 1085 (w), 1041 (m), 1024 (m), 1001 (m), 981 (s), 920 (m), 905 (w), 855 (w), 847 (w), 833 (s), 795 (w), 765 (w), 751 (m), 737 (s), 698 (s), 639 (m), 626 (w), 619 (w), 582 (w), 529 (w). Raman (460 mW, 150 scans, 25 °C, cm^{-1}): 3194 (1), 3067 (6), 3048 (3), 3028 (1), 3003 (1), 2980 (1), 2778 (1), 2583 (1), 1599 (4), 1588 (2), 1495 (1), 1451 (1), 1293 (1), 1216 (1), 1191 (2), 1164 (2), 1144 (2), 1086 (1), 1034 (4), 1005 (10), 965 (1), 936 (1), 907 (1), 859 (1), 797 (1), 745 (1), 708 (1), 679 (2), 641 (1), 622 (2), 587 (2), 531 (1), 498 (1), 483 (2), 419 (1), 408 (1), 388 (1), 359 (3), 330 (1), 290 (2), 269 (3), 248 (2), 230 (1), 207 (2), 168 (2), 147 (1), 134 (2), 114 (5), 82 (5). MS (EI, *m*/*z*, >10%): 165 (74) $[C_{13}H_9]^+$, 166 (14), 182 (13) $[H_2N(Ph)_2]^+$, 241 (15), 242 (14), 243 (100) $[CPh_3]^+$, 244 (70), 646 (1) $[M]^+$.

Crystals suitable for X-ray crystallographic analysis were obtained by slow cooling of a saturated CH_2Cl_2 solution of **16** to −20 °C.

*Silaazaheterocycle (**14**).* To a stirred solution of *N*-triphenylmethyl-*N*-trimethylsilylamine $Ph_3C-N(SiMe_3)H$ (0.700 g, 2.11 mmol) in Et_2O (10 mL) was added *n*-BuLi (2.5M, 0.89 mL, 2.22 mmol) dropwise at ambient temperature. To the resulting yellow suspension a solution of PCl_3 (0.869 g, 6.33 mmol) in Et_2O (5 mL) was added at −40 °C by syringe in one shot. The colorless suspension was warmed to ambient temperature and stirred for 4 h. The solvent was removed *in vacuo*, and the colorless residue was extracted with *n*-hexane (15 mL). After filtration (F4) the solvent was removed *in vacuo*, and CH_2Cl_2 (5 mL) was added. The pale yellow solution was concentrated to incipient crystallization *in vacuo* and stored at 5 °C, resulting in the deposition of colorless crystals. Removal of supernatant by syringe and drying *in vacuo* yielded 0.718 g (1.72 mmol, 82%) of **14** as colorless crystals. Mp: 137 °C. Anal. Calcd % (Found) for $C_{21}H_{20}Cl_2NPSi$ (416.36): C 60.58 (60.72), H 4.84 (5.26), N 3.36 (3.71). ^1H NMR (25 °C, CD_2Cl_2, 300.13 MHz): δ = 0.70 (s, 6H, CH_3), 6.98−7.13 (m, 1H, Ph), 7.19−7.47 (m. 12H, Ph), 7.50−7.64 (m, 1H, Ph). $^{13}C\{^1H\}$ NMR (25 °C, CD_2Cl_2, 75.5 MHz): δ = 3.0 (d, $^3J(^{13}C-^{31}P)$ = 2.4 Hz, C1), 84.4 (d, $^2J(^{13}C-^{31}P)$ = 30.0 Hz, C2), 126.6 (d, $^4J(^{13}C-^{31}P)$ = 3.1 Hz, C7/C10), 128.0 (s, C8/C9), 128.4 (s, C6), 128.9 (s, C5), 129.8 (d, $^4J(^{13}C-^{31}P)$ = 4.7 Hz, C4), 130.9 (s, C8/C9), 131.1 (s, C7/C10), 136.0 (d, $^3J(^{13}C-^{31}P)$ = 2.2 Hz, C11), 145.3 (d, $^3J(^{13}C-^{31}P)$ = 5.5 Hz, C3), 155.3 (d, $^3J(^{13}C-^{31}P)$ = 2.0 Hz, C12). ^{29}Si NMR (25 °C, CD_2Cl_2, 59.6 MHz): δ = 21.3. $^{31}P\{^1H\}$ NMR (25 °C, CD_2Cl_2, 121.5 MHz): δ = 187.1. IR (ATR, 25 °C, 32 scans, cm^{-1}): 3084 (w), 3056 (w), 3029 (w), 3021 (w), 3002 (w), 2976 (w), 2957 (w), 2926 (w), 2899 (w), 2853 (w), 1590 (w), 1564 (w), 1493 (m), 1459 (w), 1441 (m), 1398 (w), 1317 (w), 1281 (w), 1266 (w), 1247 (s), 1207 (m), 1184 (w), 1154 (w), 1141 (m), 1073 (m), 1018 (s), 1000 (w), 981 (m), 967 (m), 929 (m), 921 (m), 909 (w), 883 (m), 846 (s), 805 (m), 787 (s), 766 (m), 745 (s), 720 (w), 708 (m), 696 (s), 685 (w), 645 (w), 637 (w), 628 (m), 618 (w), 580 (w), 535 (w). Raman (400 mW, 250 scans, 25 °C, cm^{-1}): 3187 (1), 3158 (1), 3127 (1), 3063 (6), 3021 (1), 2978 (2), 2959 (2), 2901 (3), 2784 (1), 2583 (1), 1596 (3), 1567 (1), 1495 (1), 1461 (1), 1447 (1), 1408 (1), 1399 (1), 1320 (1), 1293 (1), 1268 (1), 1246 (1), 1189 (2), 1158 (3), 1084 (1), 1073 (1), 1036 (5), 1023 (1), 1002 (6), 969 (1), 930 (1), 909 (1), 886 (1), 876 (1), 845 (1), 793 (1), 768 (1), 743 (1), 710 (1), 699 (1), 689 (1), 647 (2), 631 (1), 620 (1), 535 (1), 504 (1), 475 (4), 458 (2), 446 (1), 435 (1), 419 (3), 392 (2), 365 (2), 325 (1), 303 (1), 282 (1), 249 (3), 215 (1), 195 (1), 167 (1), 155 (1), 124 (5), 93 (10). MS (CI^+, isobutane): 380 $[M - Cl]^+$, 416 $[M + H]^+$.

Crystals suitable for X-ray crystallographic analysis were obtained by cooling of a saturated CH_2Cl_2 solution of **14** to 5 °C.

*$[PhN(PCl_2)\text{-}PN(Ph)]_2$ (**17**).* To a stirred solution of *N*-trimethylsilylaniline, $Ph-N(SiMe_3)H$ (1.019 g, 6.16 mmol), in Et_2O (15 mL) was added *n*-BuLi (2.5M, 2.59 mL, 6.49 mmol) dropwise at ambient temperature. The resulting yellowish solution was added dropwise to a solution of PCl_3 (2.540 g, 18.48 mmol) in Et_2O (10 mL) at −80 °C over a period of 25 min. The colorless suspension was stirred at −75 °C over a period of 30 min, warmed to ambient temperature, and stirred for 1 h. The solvent was removed *in vacuo*, and the yellow residue was extracted with *n*-hexane (20 mL). After filtration (F4) the solvent was removed *in vacuo*, and the yellow oil was distilled (Kugelrohr, 10^{-3} mbar, 100 °C). To the yellowish oily residue was added CH_2Cl_2 (15 mL), and the yellowish solution was filtered (F4). The yellowish solution was concentrated to incipient crystallization *in vacuo* and stored at 5 °C, resulting in the deposition of colorless crystals. Removal of supernatant by syringe and drying *in vacuo* yielded 2.17 g (3.44 mmol, 56%) as colorless crystals which could be identified by X-ray and NMR as $[Cl_2PN(Ph)P(\mu\text{-}NPh)]_2$ (**17**). The distillate (colorless oil) could be identified by NMR as *N*-phenyl-*N*-trimethylsilylamino-*n*-butylchlorophosphane $Ph-N(SiMe_3)P(nBu)Cl$ (**18**). Data for **17** follow. Mp: 155 °C (dec). Anal. Calcd % (Found) for $C_{24}H_{20}Cl_4N_4P_4$ (630.15): C 45.75 (45.52), H 3.20 (3.26), N 8.89 (8.89). NMR (ratio *cis*:*trans* = 0:100) data for *trans* follow. ^1H NMR (25 °C, CD_2Cl_2, 300.13 MHz): δ = 6.61−6.69 (m, 4H, Ph), 6.69−6.77 (m, 4H, Ph), 7.03−7.12 (m, 2H, Ph), 7.17−7.27 (m, 4H, Ph), 7.31−7.41 (m, 6H, Ph). $^{13}C\{^1H\}$ NMR (25 °C, CD_2Cl_2, 75.5 MHz): δ = 114.9 (t, $J(^{13}C-^{31}P)$ = 9.3 Hz, Ph), 122.3 (s, Ph), 129.0 (s, Ph), 130.4 (s, Ph), 131.5 (s, Ph), 134.5 (s, C_q), 140.2 (t, $^2J(^{13}C-^{31}P)$ = 6.9 Hz, C_q). $^{31}P\{^1H\}$ NMR (25 °C, CD_2Cl_2, 121.5 MHz): δ = 157.4 (d, $^2J(^{31}P-^{31}P)$ = 483.0 Hz), 176.0 (d, $^2J(^{31}P-^{31}P)$ = 483.0 Hz). IR (ATR, 25 °C, 32 scans, cm^{-1}): 3085 (w), 3058 (w), 3031 (w), 3005 (w), 1590 (s), 1557 (w), 1538 (w), 1495 (w), 1484 (s), 1454 (m), 1447 (w), 1403 (w), 1269 (s), 1205 (s), 1176 (m), 1161 (w), 1156 (w), 1101 (m), 1074 (m), 1025 (m), 998 (w), 989 (w), 963 (m), 916 (s), 885 (m), 860 (w), 827 (s), 751 (s), 734 (w), 696 (s), 687 (s), 675 (m), 664 (m), 618 (m). Raman (460 mW, 150 scans, 25 °C, cm^{-1}): 3179 (1), 3067 (5), 3040 (2), 3009 (1), 2965 (1), 2903 (1), 2573 (1), 1644 (1), 1601 (10), 1503 (2), 1455 (1), 1401 (1), 1349 (8), 1299 (1), 1283 (1), 1208 (5), 1177 (2), 1160 (2), 1079 (1), 1036 (3), 1005 (9), 982 (5), 959 (1), 928 (1), 892 (1), 855 (1), 824 (1), 749 (1), 701 (1), 678 (3), 622 (1), 585 (3), 523 (2), 489 (3), 454 (2), 417 (1), 406 (1), 388 (4), 357 (1), 338 (1), 246 (4), 211 (5), 190 (2), 165 (2), 132 (2), 118 (2), 95 (9). MS (CI^+, isobutane): 279 $[^1/_2M - Cl]^+$, 402 $[M - N(Ph)PCl_2 - Cl + H]^+$, 436 $[M - N(Ph)PCl_2]^+$, 631 $[M - H]^+$.

Crystals suitable for X-ray crystallographic analysis were obtained by cooling of a saturated CH_2Cl_2 solution of **17** to 5 °C.

Data for **18** follow. ^1H NMR (25 °C, CD_2Cl_2, 300.13 MHz): δ = 0.20 (d, $^4J(^1H-^{31}P)$ = 1.5 Hz, $Si(CH_3)_3$), 0.82 (t, 3H, $^5J(^1H-^1H)$ = 7.3 Hz, CH_3), 1.24−1.63 (m, 6H, CH_2), 7.03−7.11 (m, 2H, *o*-Ph), 7.18−7.37 (m, 3H, *m*/*p*-Ph). $^{13}C\{^1H\}$ NMR (25 °C, CD_2Cl_2, 75.5 MHz): δ = 0.8 (d, $^3J(^{13}C-^{31}P)$ = 9.2 Hz, $Si(CH_3)_3$), 14.1 (s, CH_3), 24.3 (d, $^3J(^{13}C-^{31}P)$ = 14.1 Hz, CH_2), 26.6 (d, $^2J(^{13}C-^{31}P)$ = 22.1 Hz, CH_2), 36.4 (d, $^1J(^{13}C-^{31}P)$ = 32.1 Hz, CH_2), 126.5 (s, *p*/*m*-Ph), 129.2 (s, *p*/*m*-Ph), 129.9 (d, $^3J(^{13}C-^{31}P)$ = 4.0 Hz, *o*-Ph), 142.5 (d,

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$^2J(^{13}C-^{31}P)$ = 8.7 Hz, C_q). ^{29}Si NMR (25 °C, CD_2Cl_2, 59.6 MHz): δ = 14.7. $^{31}P\{^1H\}$ NMR (25 °C, CD_2Cl_2, 121.5 MHz): δ = 142.1.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details, a table of crystal data, list of selected bond lengths and angles, and crystallographic information files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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